THE EFFECT OF THE CHEMICAL COMPOSITION OF CIRCONIUM AND NIOBIUM CARBIDES IN THE HOMOGENEITY REGION ON THEIR ELECTRIC AND THERMAL PROPERTIES

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THE EFFECT OF THE CHEMICAL COMPOSITION OF ZIRCONIUM AND NIOBIUM   /2375*

CARRIERS IN THE HOMOGENEITY REGION ON THEIR ELECTRIC AND

THERMAL PROPERTIES

V. S. Neshpor, S. S. Ordan'yan,

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ABSTRACT

The electrical and thermal properties of monocarbides

of the IV and V group monocarbides are investigated, and

differences between carbides associated with the electron

collective state, resulting from differences in effective

valences of transition metals, are found. Properties of

these carbides show similarities in lattice dynamics.

The refractory carbides of the IV and V group of metals display metallic

properties (ref. 1) and present a great interest as materials for certain parts

of termoelectric transducers. In the work of Bowman (ref. 2) it was reported

that zirconium carbide is used for production of cathodes for thermoionic

transducers. The electric and thermophysical properties of transition

metal carbides were recently investigated by a number of authors (ref. 3);

however, there is only a limited number of investigations of the   /2376

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*Numbers given in the margin indicate the pagination in the original foreign

text.

dependence of these properties on the carbon content of these phases (refs. 4-6) and in the majority of cases the reported properties of carbides are more ~~of~~ or less randomly ascribed to stoichiometric composition.

TABLE 1. BOUND CARBON CONTENT IN NIOBIUM AND ZIRCONIUM CARBIDES AND SOME PROPERTIES OF THE INVESTIGATED COMPOSITIONS.

Металлический компонент	Содержание связанного углерода (атомн. %)	Состав фазы, MeC$_x$	Электросопротивление ($\Omega \cdot$ см)·10^{-6}	Теплопроводность (W/м · град.)	Термоэдс (μV/град.)
1	2	3	4	5	6
Nb	47.6	NbC$_{0.908}$	89.8	11.2±0.7	−5.5+0.3
	46.1	NbC$_{0.855}$	135.2	10.7±1.6	−5.8±0.6
	44.7	NbC$_{0.808}$	151.9	10.2±1.2	−3.4±0.4
	43.15	NbC$_{0.759}$	150.0	9.7±0.7	−2.1±0.1
	41.5	NbC$_{0.710}$	171.7	9.0±0.7	−1.9±0.1
Zr	47.4	ZrC$_{0.903}$	100.0	11.6±1.0	−6.3±0.3
	45.0	ZrC$_{0.820}$	123.6	10.3±1.0	−3.7±0.3
	43.0	ZrC$_{0.756}$	130.2	11.0±0.3	−2.5±0.6
	41.8	ZrC$_{0.718}$	135.0	9.4±0.9	−0.7±0.2
	38.6	ZrC$_{0.628}$	166.2	8.2±0.9	+0.1±0.3

Col. 1 - Metal component
2 - Bound carbon content (atom. %)
3 - Composition of MeC$_x$ phase
4 - Electric resistance ($\Omega \cdot$ cm)·10^{-6}
5 - Thermal conductivity (W/m·deg)
6 - Thermal emf (μV/deg)

In this work we investigated electric conductivity, thermal conductivity and thermal emf of zirconium and niobium carbides (ZrC_x and NbC_x) in the region of their homogeneity at $0.6 - 0.7 \leqslant x \leqslant 1$. The carbide specimens were prepared by pressing and sintering of powder mixtures close to stoichiometric composition of carbide and appropriate metals (ref. 7). Sintering was carried out in a TVV-4 vacuum furnace at $10^{-4} - 10^{-5}$ mm pressure and $2200 - 2400°$ C. The content of bound carbon in alloys is given in Table 1. The porosity of the obtained samples was 5-15 percent. Figure 1 shows carbide specimens.

X-ray diffraction analyses have shown that all these alloys consist of a single phase and have face-centered cubic NaCl type lattice. The lattice periods are smoothly decreasing with decrease of the carbon content in this phase from 4.455 kX for $NbC_{0.908}$ to 4.~~623~~ .423 kX for $NbC_{0.710}$ and from 4.673 kX for $ZrC_{0.903}$ to 4.648 kX for $ZrC_{0.628}$ with slight positive deviation ~~form~~ from a straight line relationship.
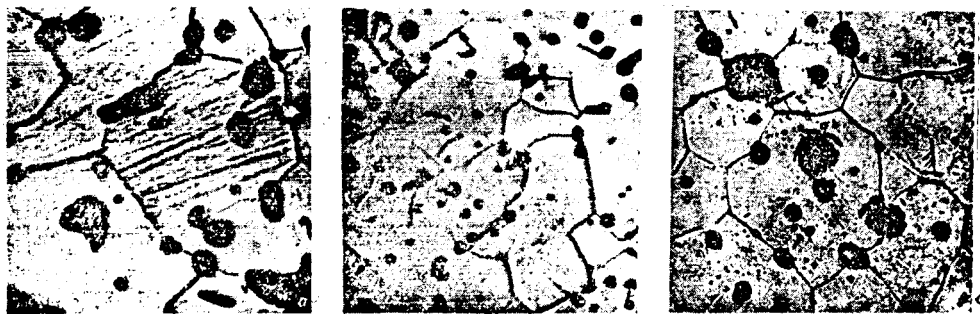
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Figure 1. Microstructure of some of the investigated alloys; a--$ZrC_{0.903}$, b--$ZrC_{0.623}$, c--$NbC_{0.808}$ etched in HNO_3+HF, magnification 800 x.

Measurements were made of the resistivity, absolute differential thermal emf and thermal conductivity coefficient on the obtained specimens at room temperature. The resistivity measurements were done by the d.c. compensation method. The correction for porosity of specimens was done using the Odelevskiy formula (ref. 8). The obtained values of resistivity of alloys are given in Table 1.

The error of measurements, including porosity correction, comprises 6 percent. The thermal conductivity of specimens was measured by the stationary thermal flux method using the device in which the determination of the thermal flux is done by means of thermal emf, developed by parallel plates made of a semi-conductor between which the measured specimen is inserted. The same set-up was used for the determination of the absolute differential thermal emf using the alumel branch of the chromel-alumel thermocouples as the reference electrode. The temperature gradient was measured between the hot and the cold ends of the specimen.

The correction for the effect of the porosity of specimens on the thermal conductivity coefficient was introduced by means of a simple relationship (ref. 9)

$$\lambda_0 = \frac{\lambda_P}{(1 - P)},$$

where λ_0 and λ_P represent thermal conductivities of solid and porous specimens respectively, and the porosity of the porous specimen is represented by P.

The obtained values of thermal conductivity coefficients and thermal emf for the investigated alloys are shown in Table 1.
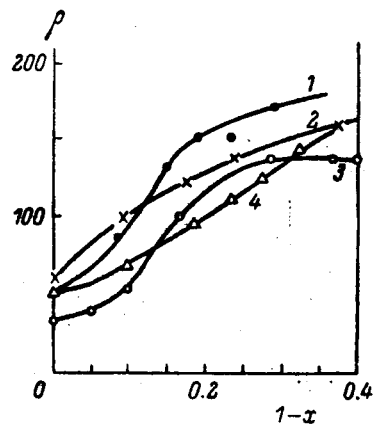

Figure 2. Resistivity ρ ($\mu\Omega \cdot cm$) as a function of carbide

content (1 - x) carbides: 1 - NbC_x, 2- ZrC_x, 3- TaC_x

(ref. 5), 4- TiC_x (ref. 4).

Figure 2 shows the relationship of the electrical conductivity of ZrC_x and NbC_x carbides and the carbon content in carbide phases. This latter quantity is expressed as (1 - x), the deficiency of carbon in the MeC_x formula as compared with stoichiometric composition of $MeC_{1.0}$. The comparison of the same graphs shows the appropriate relationships for TiC_x (ref. 4) and TaC_x (ref. 5). Our attention is drawn to the fact that with increase of (1 - x) the electrical

conductivity of carbide of the IV group of metals (Ti, Zr) increases almost linearly, while the carbides of the V group of metals (Nb, Ta) a more complex practically parabolic relationship is noted. The increase of the electrical conductivity of MeC_x carbides with decrease of the content of carbon in them, the results on one hand in scattering of current carriers to vacancies in the carbon sublattice, while on the other hand it results in the increase of the cross section of thermal scattering of current carriers due to decrease of the interatomic bond strength. This is indicated in figure 3 by decrease of the modulus of elasticity $M_{red}\ \theta^2$ of carbide phase of the MeC_x composition with increase of $(1 - x)$. Here M_{red} represents the reduced molecular weight of metal and carbon considering their relative content in MeC_x "molecule" and θ is characteristic temperature, calculated from the melting point and the average principal quantum number of the components of the alloy. The decrease of the strength of interatomic bonds in MeC_x alloys with the decrease of carbon content is also indicated by the increase of thermal expansion characteristics.*

Neglecting the residual electrical resistance in the absence of carbon vacancies, the resistivity of MeC_x alloys (ρ) may be represented in the form

$$\rho_T = \rho - \rho_V, \qquad (1)$$

where ρ_T and ρ_V are electrical resistances due to the scattering of current carriers on thermal vibrations and on carbon vacancies respectively.

The accurate calculation of ρ_V is an extremely complex problem. In order to approximate this quantity use is made of quantity $\Delta\rho'_V = 20\ \mu\Omega\cdot cm/at.$ percent

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*Thus, for instance, for $\overset{Nb}{MeC_x}$ carbides the thermal expansion coefficient increases from $6.2\cdot10^{-6}$ deg for $NbC_{0.98}$ to $6.8\cdot10^{-6}$ deg^{-1} for $NbC_{0.7}$.
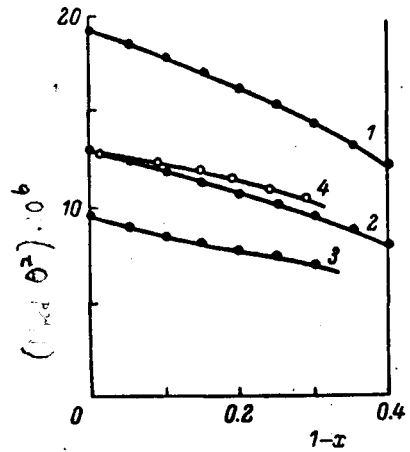
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Figure 3. Modulus of elasticity $[(M_{red}\,\theta^2)\cdot10^6]$ of carbides as a function of their composition $(1 - x)$; carbides: 1- TiC_x, 2- ZrC_x, 3- TaC_x, 4- NbC_x.

of the vacancies reported in reference 16 for the increase of the electrical resistance of metallic niobium at the expense of vacancies in the lattice nodes of Nb. Since the scattering cross section, determined by the lattice defect of the radius r, is proportional to r^2 (ref. 17) we may assume that

$$\frac{\Delta\rho_{\bullet V}^{(C)}}{\Delta\rho_{\bullet V}^{(Nb)}} \simeq \left(\frac{r_C}{r_{Nb}}\right)^2,$$

where r_C/r_{Nb} is the ratio of the atomic radii of carbon and niobium. From this ratio we obtain $\Delta\rho_V^{(C)} \simeq 5\ \mu\Omega\cdot cm$/at percent of carbon vacancies and we assume that this quantity is approximately the same for all of the considered MeC_x carbides. According to the Nordheim rule (ref. 17) at low concentrations of impurities (up to 20 at. percent; in this case carbon vacancy impurities) in formula (1).

$$\rho_V = c_V\,\Delta\rho_V^{(C)},$$

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where c_v is the concentration of carbon vacancies.

Due to thermal changes the electrical resistance of metal substances depends on the density of the state q (ϵ) in the conducting zone, the velocity of current carriers V(ϵ) and the relaxation time τ (ϵ, M θ^2, T) (ref. 18).

$$\rho_T = \frac{l^2}{3} \cdot V^{-2} \cdot (\epsilon) \, q^{-1}(\epsilon) \, \tau^{-1} \cdot (\epsilon, M\theta^2, T)$$

(2)

At constant temperature

$$\rho_T \cdot M\theta^2 = f(\epsilon).$$

(3)

In regard to f(ϵ) one may say only that for real metals it is apparently a power function of the energy of electrons ϵ (ref. 19). The accurate determination of $f(\epsilon) \sim \epsilon^{-3}$ is possible only in the cases of free electrons and in the presence of only one zone. Combining equations (1) and (3) we obtain

$$f(\epsilon) = (\rho - \rho_v) \, M_{red} \theta^2.$$

(4)

Figure 4 shows the dependence of $(\rho - \rho_v) \cdot M_{red} \, \theta^2$ on the deficiency of carbon in MeC$_x$ carbides of Zr, Nb, Ti and Ta.

It can be seen that this quantity which depends on the state of electron conductivity is a decreasing function of the content of metals of the IV group (Ti, Zr) in carbides and passes through a maximum which is located in the homogeneity region of carbides of group V metals (Nb, Ta).

The position of this maximum is not rigorously obeyed as it depends on the accuracy of the evaluation of $\Delta\rho_v^{(c)}$ which in this work is done very approximately. However, the observed difference in the concentration dependence of function (4) for carbides of the IV and V groups is very characteristic and it indicates the significant difference of the nature of the electron structure of
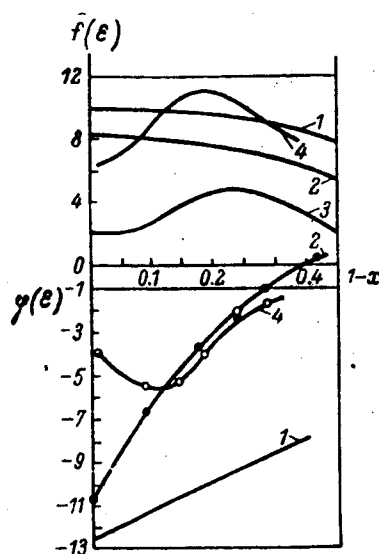
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Figure 4. Dependence $f(\epsilon) = [(\rho - \rho_v) M \theta^2] \cdot 10^8$

and $\varphi(\epsilon) \approx \alpha(\mu\Gamma/deg)$ on composition of carbides

$(1 - x)$. carbides: 1- TiC_x, 2- ZrC_x, 3- TaC_x,

4- NbC_x.

carbides of groups IV and V despite their crystallographic similarity which was noted earlier during the comparison of the thermodynamic properties (ref. 20) and during the investigation of the possible number of neighboring carbon vacancies in the carbide lattice (ref. 21). It was shown in ref. 22 that the maximum metallic valence of transition metals is approximately 5.8. According to refs. 23 and 24 carbon atoms in carbides transfer part of their valence electrons to fill electron defects in the unfilled d-shells of metals, thus increasing its effective valence. One may assume that carbon atoms are capable of transferring not more than one outer electron, if one considers the magnitude of their first and second ionization potential. In such a case in carbides of group IV metals even with maximum content of carbon ($MeC_{1.0}$) the valence of metal ($\leqslant 5$) is not maximal, and when the carbon content is lowered the number of metal bonds, formed

by the electron collective, their energy ϵ and $f(\epsilon)$ decrease. In the case of

group V metal carbides during stoichiometric composition $MeC_{1.0}$ the valence

metal ($\leqslant 6$) is apparently greater than the maximum possible valence 5.8, and

the excess electrons occupy the antibonding state. In all probability this

results in the shift of the upper boundary of the homogeneity region of group

V carbides towards a lowered content of carbon than $MeC_{1.0}$. This shift increases

with increase of the acceptor ability of the d-shell of metal (refs. 23, 25) from

TaC_x to VC_x (refs. 13, 14, 26). Consequently, it is worthwhile to note that

transition metals of the IV group do not form stable monocarbides with NaCl

structure at all (ref. 3). If one considers that the carbon atom in carbides

contributes approximately one electron then the maximum metallic valence in

carbides of group V and the appropriate maximum of $f(\epsilon)$ will be reached when the

composition of carbide is $MeC_{\sim 0.8}$, i.e., inside the homogeneity region of the

$Me^V C_x$ phase, which in fact is observed on graphs showing $f(\epsilon) = (\rho - \rho_v) \cdot M \, \theta^2$

as a function of $(1 - x)$ (fig. 4). On the basis of these developed concepts it

is possible to find an explanation for the fact that in $4TaC \cdot HfC$ and $4TaC \cdot ZrC$

$(Ta_{0.8} Hf_{0.2}C$ and $Ta_{0.8} Zr_{0.2}C)$ solid solutions with effective metallic valence

of approximately 5.8 a maximum melting point is obtained (ref. 27).

The thermal emf, α , metallic systems with degenerate current carriers

is determined by the following relationship (ref. 28)

$$\alpha = \mu \cdot \ln T = \frac{c_{el}}{e} \left\{ 1 + \frac{2}{3} \left[\frac{d \lg \tau (\epsilon)}{d \lg \epsilon} \right]_{\epsilon_0} \right\} \ln T \qquad (5)$$

where $c_{el} \sim q(\epsilon)$ (ref. 29) is the capacity of current carriers and a derivative

of the log is taken on the Fermi surface (ϵ_F). Since $q(\epsilon)$ and $\tau(\epsilon)$ are power

functions of energy electrons (refs. 17 - 19) at constant temperature one may

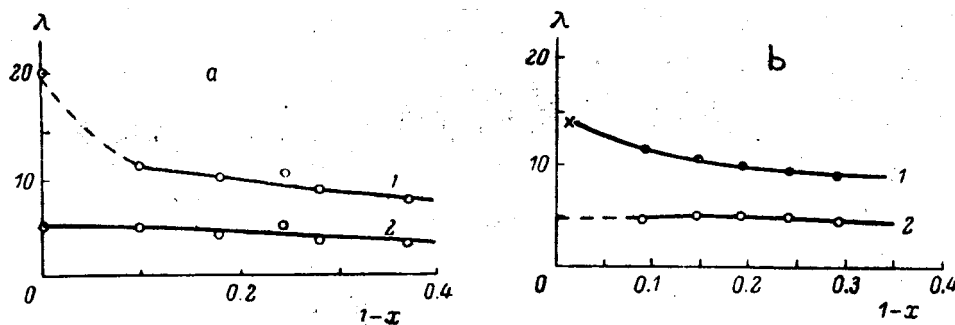write $\alpha \sim \varphi(\epsilon)$--the power function of energy. Figure 4 shows the relationship

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Figure 5. Thermal conductivity (λ, W/m·deg) as a function
of composition of carbide (1 - x); thermal conductivity:
1--total, 2--lattice; a--ZrC_x, b--NbC_x.

of the thermal emf of MeC_x carbides (Me $\approx$ Zr, Nb, Ti) to composition (1 - x).
It is apparent that the concentration dependence of φ (ϵ) $\sim \alpha$ and f (ϵ), de-
rived from electrical resistance, for the same carbides are qualitatively the
same and thus support the above indicated difference between the carbides of
metals of group IV and group V.

The dependence of thermal conductivity of ZrC_x and NbC_x carbides on the
composition is indicated in Figure 5, a and b. Using the well known Wiedemann-
Franz relationship (ref. 17), the lattice thermal conductivity λ_{lat} was cal-
culated for substances and it is also shown in figure 5. It is apparent that
λ_{lat} is almost independent of the carbon content in carbides displaying only
a slight decrease with increase of the carbon deficiency.

According to the data of reference 30 the lattice thermal conductivity
of cubic crystals is a function of energy U and the interatomic distance r in
the following manner:

$$\lambda_{lat} = \frac{const}{T \sqrt{M}} \cdot \frac{u^{3/2}}{r^2} , \qquad (6)$$

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where M is the mean mass of atomic components.

Using the relationship of lattice energy and interatomic distances in Me_x compounds as a function of the valence of the components f and the atomic number, derived by Sarkisov in reference 31 we may write:

$$u = \frac{\text{const}\ \left(a_{Me} f_{Me} + a_x f_x\right)^{1/3}}{\left(F_{Me}^{1/3} + F_x^{1/3} + F_f^{1/3}\right)},$$

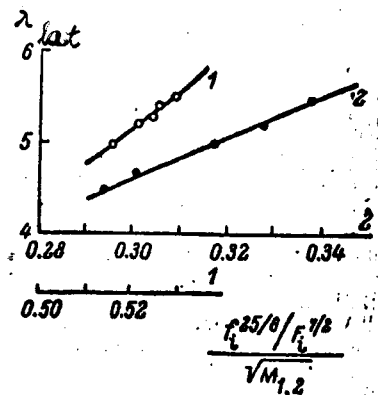$$r_0 = \frac{\text{const}'\ \left(F_{Me}^{1/3} + F_x^{1/3} + F_f^{1/3}\right)}{\left(a_{Me} f_{Me} + a_x f_x\right)^{1/3}}$$

Figure 6. λ_{lat} (W/m x deg) as a function of

$$\frac{f_i^{25/6}}{\sqrt{M} \cdot F_i^{7/2}} \cdot \quad 1\ \text{--NbC}_x,\ 2\text{--ZrC}_x.$$

For this type of structure at constant temperature we may rewrite equation (6) in the form

$$\lambda_{lat} = \frac{\text{const}}{\sqrt{M}} \cdot \frac{f_i^{25/6}}{F_i^{7/2}}, \tag{7}$$

where $f_i = a_{Me} f_{Me} + a_C f_C$ and $F_i = F_{Me}^{1/3} + F_C^{1/3} + F_f^{1/3}$ [f_{Me} and f_C are the number of valence electrons for the metal and carbon (4 for Zr and C and 5 for Nb),

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$F_{Me,C} = a \cdot (z_{MeC} - f_{MeC})$ and $F_f = F_i^{2/3}$; z is the atomic number of the component; a is its atomic fraction in the compound]

Table 2 shows the values of function $\dfrac{f_i^{25/6}}{\sqrt{M} \cdot F_i^{7/2}}$ for ZrC_x and NbC_x carbides in the region of their homogeneity.

TABLE 2.   VALUES OF $\dfrac{f_i^{25/6}}{\sqrt{M} \cdot f_i^{7/2}}$ FOR ZrC_x AND NbC_x.

Phase	$\dfrac{f_i^{25/6}}{\sqrt{M} \cdot F_i^{7/2}}$	Phase	$\dfrac{f_i^{25/6}}{\sqrt{M} \cdot F_i^{7/2}}$
$ZrC_{1.0}$	0.337	$NbC_{1.0}$	0.529
$ZrC_{0.9}$	0.327	$NbC_{0.9}$	0.525
$ZrC_{0.8}$	0.318	$NbC_{0.8}$	0.524
$ZrC_{0.7}$	0.301	$NbC_{0.7}$	0.522
$ZrC_{0.6}$	0.295	$NbC_{0.6}$	0.516

It is apparent that function $\dfrac{f_i^{25/6}}{\sqrt{M} \cdot F_i^{7/2}}$ which determines the lattice thermal conductivity in equation (7) is very slowly decreasing with increase of the carbon deficiency $(1 - x)$ (by 2 percent within the limits of homogeneity region of NbC_x and 12 percent within the homogeneity region of ZrC_x). This corresponds to the observed insignificant decrease of the lattice thermal conductivity (5 percent within the limits of the homogeneity region of NbC_x and 12 percent within the limits of the homogeneity region of ZrC_x).

Figure 6 shows a direct proportionality between λ_{lat} and $\dfrac{f_i^{25/6}}{\sqrt{M} \cdot F_i^{7/2}}$ which supports the applicability of formulas (6) and (7) to the considered phases of variable composition.

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Conclusions

The investigations of the electrical and thermal properties of monocarbides of metals in the IV and V groups have shown that there is a significant difference between those properties of $Me^{IV}C_x$ and $Me^V C_x$ carbides which are associated with the state of the electron collective in ~~this~~ these substances and apparently results from a difference in the effective valence of the transition metals of these groups. At the same time carbides of $Me^{IV}C_x$ and $Me^V C_x$ carbides display a similarity with respect to properties which are associated with lattice dynamics--modules of elasticity $Me\,\theta^2$, lattice thermal conductivity and the thermal expansion coefficient.

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REFERENCES

1. Samsonov, G. V. and Umanskiy, Ya. S. Solid Compounds of Refractory Metals (Tverdyye soyedineniya tugoplavkikh metallov) State Metallurgical Publishing House (Metallurgizdat), Moscow, 1957.

2. Bowman, M. Transformation of Heat and Chemical Eenergy into Electrical Energy in Rocket Systems (Preobrazovaniye tepla i khimicheskoy energii v elektroenergiyu v raketnykh sistemakh) Foreign Literature Publishing House (IL), p. 128, 1963.

3. Samsonov, G. V. Refractory Compounds (Tugoplavkiye soyedineniya) Metallurgizdat (State Metallurgical Publishing House), Moscow, 1963.

4. L'vov, S. N., Nemchenko, V. F. and Samsonov, G. V. Poroshkovaya Metallurgiya, Vol. 4, p. 3, 1962.

5. Samsonov, G. V., Rukina, V. D. Dopovidi AN URSR, Vol. 3, p. 247, 1957.

6. Meyerson, G. A., Kotel'nikov, R. B. and Bashnakov, S. N. Atmonaya energiya, Vol. 9, p. 387, 1960.

7. Averbe, R. G., Avgustinik, A. I., Vil'k, Yu. N. and Ordan'yan, S. S. Abstracts of Reports of the Scientific and Technical Conference of the Leningrad Institute of Technology, imeni Lensovet (Tezisy dokladov nauchno-tekhicheskoy konferentsii LTI Im. Lensoveta), Goskhimizdat (State Chemical Publishing House), 1962.

8. Odelevskiy, V. I. Zhurnal Tekhnicheskoy Fiziki (ZhTF), Vol. 21, p. 682, 1951.

9. Lorb, A. J. Am. Ceram. Soc., Vol. 37, No. 2, p. 96, 1954.

10. Cadoff, I. and Nielsen, I. J. Met., Vol. 5, p. 248, 1963.

11. Averbe, R. G., Avgustinik, A. I., Vil'k, Yu. N., Kondrashev, Yu. D., Nikol'skiy, S. S., Omel'chenko, Yu. A. and Ordan'yan S. S. Zhurnal prikladnoy khimii (Zh. PKh) Vol. 35, p. 1976, 1962.

12. Benesovsky, F. and Rudy, E. Planseeber. f. pulvermet., Vol. 8, p. 66, 1960.

13. Storms, E. and Krikorian, N. J. Phys. Chem., Vol. 64, p. 1471, 1960.

14. Ellinger, F. Trans. Am. Soc. Met., Vol. 31, p. 89, 1943.

15. Oshcherin, B. N. Poroshkovaya metallurgiya, Vol. 1, p. 11, 1962.

16. Gergory, D. Acta Metallurg., Vol. 6, p. 623, 1953.

17. Mott, N. and Jones, H. The Theory of the Properties of Metals and Alloys, Oxford, 1936.

18. Wilson, A. H. The Theory of Metals, second ed., Cambridge, 1954.

19. Kolomoyets, N. V. ZhTF, Vol. 28, p. 936, 1958.

20. Averbe, R. G. and Nikol'skiy, S. S. Teplofizika vysokikh temperatur, Vol. 1, p. 39, 1963.

21. Tskhay, V. P. and Geld, P. V. Fizika metallov i metallovediniye (FMM), Vol. 16, p. 493, 1963.

22. Pauling, L. Proc. Roy. Soc., Vol. A196, p. 343, 1949.

23. Samsonov, G. V. Dokaldy Akademii nauk SSSR (DAN SSSR) Vol. 93, p. 689, 1953.

24. Neshpor, V. S. Refractory Cermet Materials (Vysoko-temperaturnyye metallokeramicheskiye materialy), Izd. AN USSR, Publishing House of the Academy of Sciences of the Ukrainian SSR, Kiev, p. 46, 1962.

25. Samsonov, G. V., Neshpor, V. S. and Kudintseva, G. A. Radiotekhnika i elektronika, Vol. 2, p. 632, 1957.

26. Storms, E. and McNeal, R. J. Phys. Chem., Vol. 66, p. 1401, 1962.

27. Agte, C. and Alterthum, H. Z. Techn. Phys., Vol. 6, 1930.

28. McDonald, Z. Phys. Chem., (BDR), Vol. 16, p. 310, 1958.

29. Zeyts, F. Modern Solid State Theory (Sovremennaya teoriya tverdogo tela) Gostekhizdat, State Technical Publishing House, Moscow, p. 169, 1949.

30. Kontorova, T. A. ZhTF, Vol. 26, p. 9, 1956; Vol. 28, p. 8, 1958.

31. Sarkisov, E. S. ZhFKh, Vol. 28, p. 627, 1954; Vol. 37, p. 396, 1963.